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VIOLET/ULTRAVIOLET SEMICONDUCTOR INJECTION LASERS USING GaN-BASED MATERIALS

Cornell University

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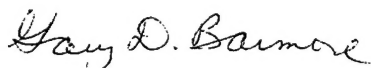
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13. ABSTRACT (Maximum 200 words) The GaN material system was examined for the growth of semiconductor injection lasers for high density optical interconnect applications. The effort focused on the growth, via molecular beam epitaxy, of GaN buffers and epitaxial layers on sapphire substrates. Substrate temperature, growth rate, and nitrogen power and flow rate were varied during buffer and epilayer growth to determine optimal parameters. RGA source pressures, RHEED, and substrate temperature, were monitored during growth, followed by mobility, photoluminescence, and X-ray measurements for good samples. The best recipe involved low temperature, low buffer growth rate followed by high temperature buffer anneal, followed by higher temperature, high mobility quality epilayer growth. Mobilities as high as 200 cm ² /V sec were measured. However, due to the lack of a matching substrate, the high defect densities obtained precluded the demonstration of a lasing structure.				
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Violet/Ultraviolet Semiconductor Injection Lasers Using GaN-Based Materials

Abstract

Violet and ultra-violet lasers made from GaN have useful properties for optical interconnects and data storage. The topic of this investigation has been fabrication of lasers operating at near-UV wavelengths. The development of lasers made from GaN requires greater control of the materials synthesis than presently exists. A problem in this synthesis is the lack of an ideal substrate for epitaxial growth. Most of the effort reported here has focused on the growth of GaN by molecular beam epitaxy (MBE), and understanding how lattice mismatched growth has affected the epitaxial layer properties. Actual lasers could not be fabricated because of inadequate material perfection. The materials development reported here shows significant advancement in understanding the growth of GaN for laser applications.

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Background

The future packing density of optical interconnects will require shorter wavelength lasers than presently exist. Optical storage will similarly benefit from smaller diffraction limited spot sizes at shorter wavelengths. The only direct bandgap semiconductors which can emit light in the UV wavelength regions are the III-nitrides; GaN and compounds of AlGaN.

These III-nitrides are difficult to synthesize for two reasons. First, a lattice matched substrate does not exist. This problem leads to high defect densities which reduce optical recombination efficiencies and thereby reduce the prospect of successful laser operation. The second difficulty is delivering nitrogen to the growing wafer surface in a form which will incorporate into GaN when growth takes place by MBE.

Growth of GaN by MBE

Nucleation layer development

All GaN materials grown for this program came from a molecular beam epitaxy (MBE) machine which has been configured for growth of nitrides. A schematic of the MBE machine, as it was configured at the end of the program, is seen in Figure 1. Conventional thermal sources are used for the group III elements and dopants. All of the growths for this program were performed with the Oxford remote RF plasma source of atomic nitrogen. At the end of the program, the EPI RF nitrogen source was added. A quad mass analyzer was installed in a furnace port to monitor desorbed species during growth. The sapphire substrates are mounted indium-free using the technology reported in the last ES&E.

Efforts to improve MBE growth of GaN have shown significant progress during this ES&E. A focus of these efforts is optimization of the nucleation layer on sapphire. Evaluation of GaN for laser applications was primarily through Hall mobility measurements and photoluminescence (PL). The highest mobilities and strongest PL obtained during this program came from using GaN nucleation layers grown at low substrate temperatures relative to temperatures used for growth of higher quality GaN layers which follow. High substrate temperatures cannot be used for nucleation of GaN because it does not stick to sapphire. Significant improvement in growth rates were also obtained by using a more efficient source of atomic nitrogen.

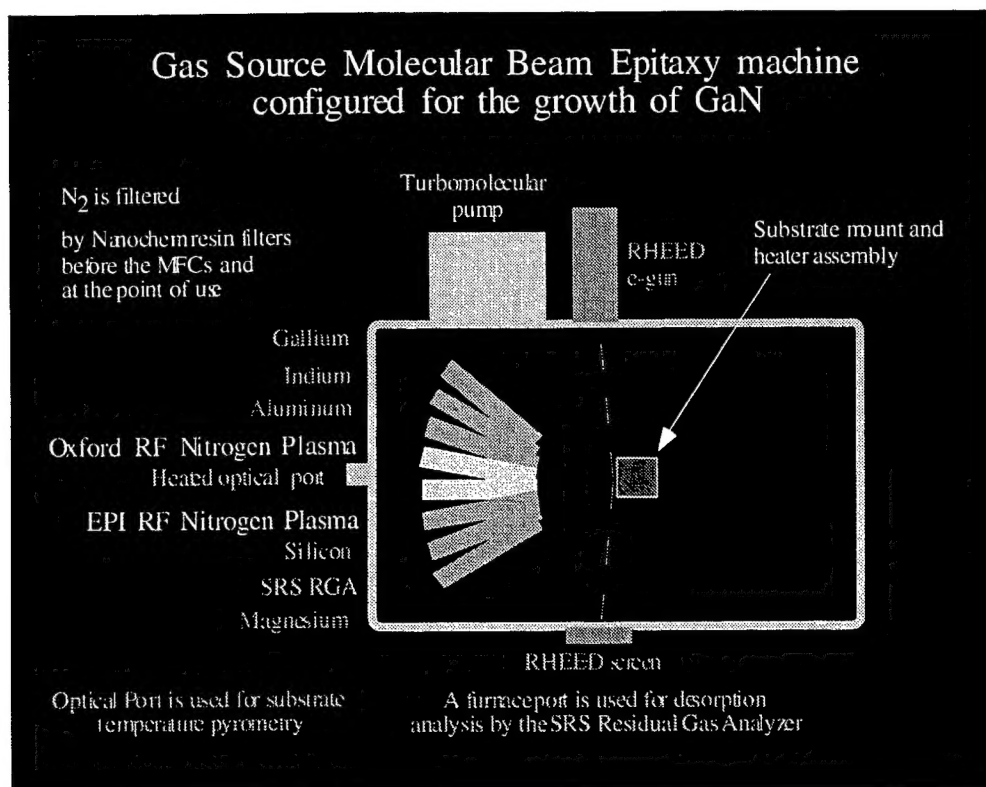


Figure 1 Diagram of MBE machine used for growth of III-nitrides

Optimization of substrate temperature

Optimization of growth conditions included studies of varying the substrate temperature, growth rate and nitrogen RF power and flow for both the nucleation layer and the higher quality epitaxial layer for laser applications. In Figure 2 variation of mobility with substrate temperature of n-GaN doped at $1 \times 10^{18} \text{ cm}^{-3}$ can be seen. Data is shown as a function of temperature as measured by both the substrate heater thermocouple and the optical pyrometer. During the last ES&E, it was found that the temperature of the metallization on the back of the sapphire wafer could be monitored by an optical pyrometer. Although this temperature measurement is still not accurate, it provides better reproducibility than using the heater thermocouple.

The mobilities are greatest for growths at the highest substrate temperatures. Higher temperatures than those investigated are not presently practical. They are beyond the limit which the substrate heater assembly can tolerate without shortening its lifetime to a few months (experimentally

determined under this program). The few growths attempted at higher temperature failed for various reasons including substrate cracking, slippage, or completely falling out of the substrate holder. The highest mobilities of more than 200 cm^2/Vsec are among the best reported for intentionally doped GaN by any growth technique. Higher mobilities are seen in OMVPE grown undoped GaN with comparable free concentration density, but not in doped GaN.

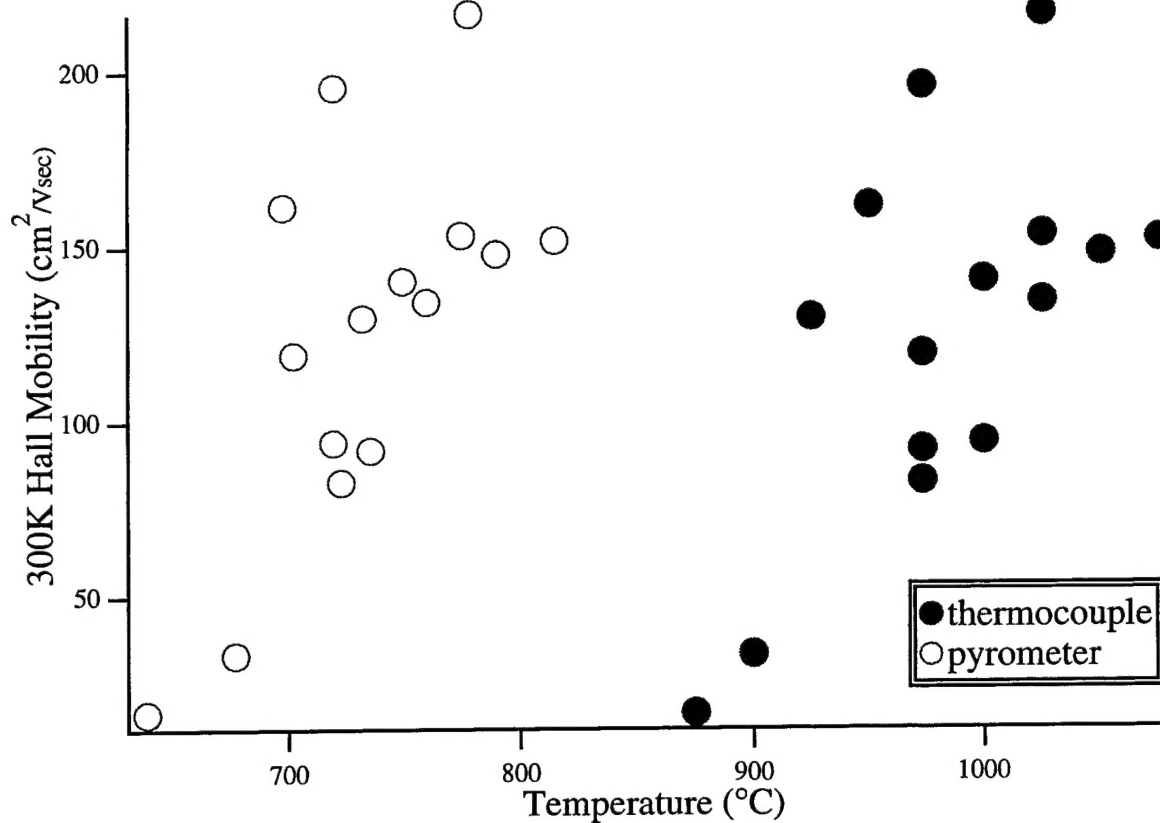


Figure 2 Mobility of n-GaN as a function of thermocouple and pyrometer temperatures

Another feature of Figure 2 is the wide range of mobilities obtained at a single growth temperature. Variations are due to slight differences in the nucleation layer growth conditions, RF source PBN liner erosion (see below), and uncontrolled reproducibility variations of unknown origin. The deviation of mobility values shown is somewhat typical of other parametric studies that were conducted.

All of the growths shown in Figure 2 were made on 1/4 of 2 inch diameter sapphire substrates. When two of the growth conditions shown in Figure 2 were employed for growth on entire 2 inch

diameter wafers, mobilities greater than $200 \text{ cm}^2/\text{Vsec}$ were routinely obtained. In all, 6 growths with mobilities greater than $200 \text{ cm}^2/\text{Vsec}$ were obtained just after the end of the program - all on 2 inch wafers only. There has been only one wafer of almost 500 grown on 1/4 wafer that was had a mobility beyond $200 \text{ cm}^2/\text{Vsec}$. The reason for this observation has not been determined.

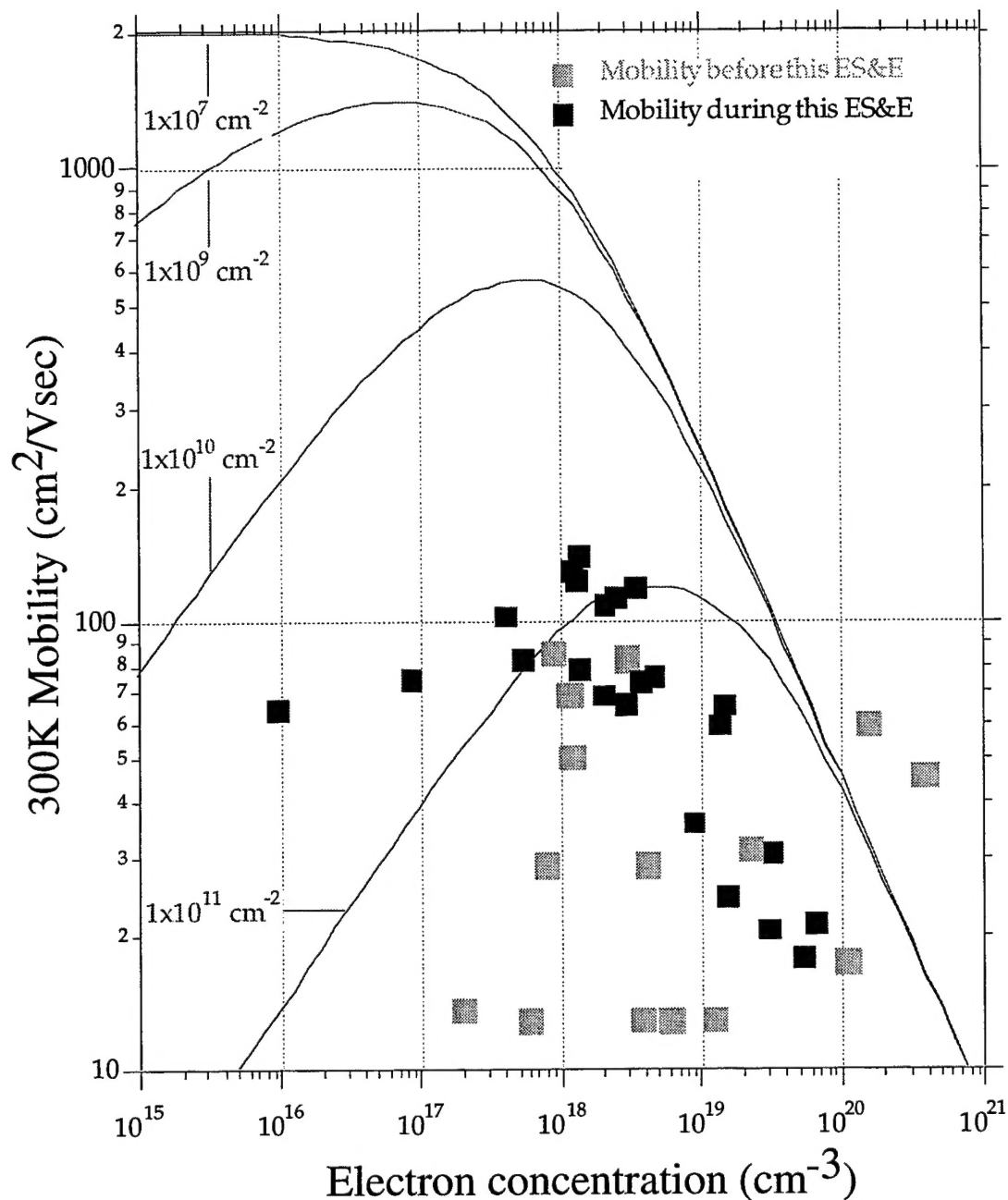


Figure 3 Electron mobility as a function of carrier density. Theoretical curves of mobility limits as a function of defect density are shown for reference

A summary of MBE mobilities for GaN:Si obtained prior to, and during, this program are seen in Figure 3. The early mobilities obtained with the Oxford Applied Research CARS-25 remote RF plasma source of atomic N are among the lowest values due to use of poor nucleation layers. Progress in nucleation layer development took place during this past year as seen in Figure 3. Higher mobilities were obtained as a result of lower defect densities which produced less electron scattering. The theoretical curves developed during this year are also shown. The effect of defects on mobility are clear. Highest mobilities require lowest defect densities.

Nitrogen to Ga optimization

There are several process variables to be optimized for GaN growth by MBE. They include substrate temperature, nitrogen pressures and flows, plasma RF power and growth rate. We have found that these parameters are significantly interrelated. Figure 4 shown below describes the relationship between N/Ga ratio and substrate temperature on surface morphology and RHEED observations of the GaN surface during MBE growth.

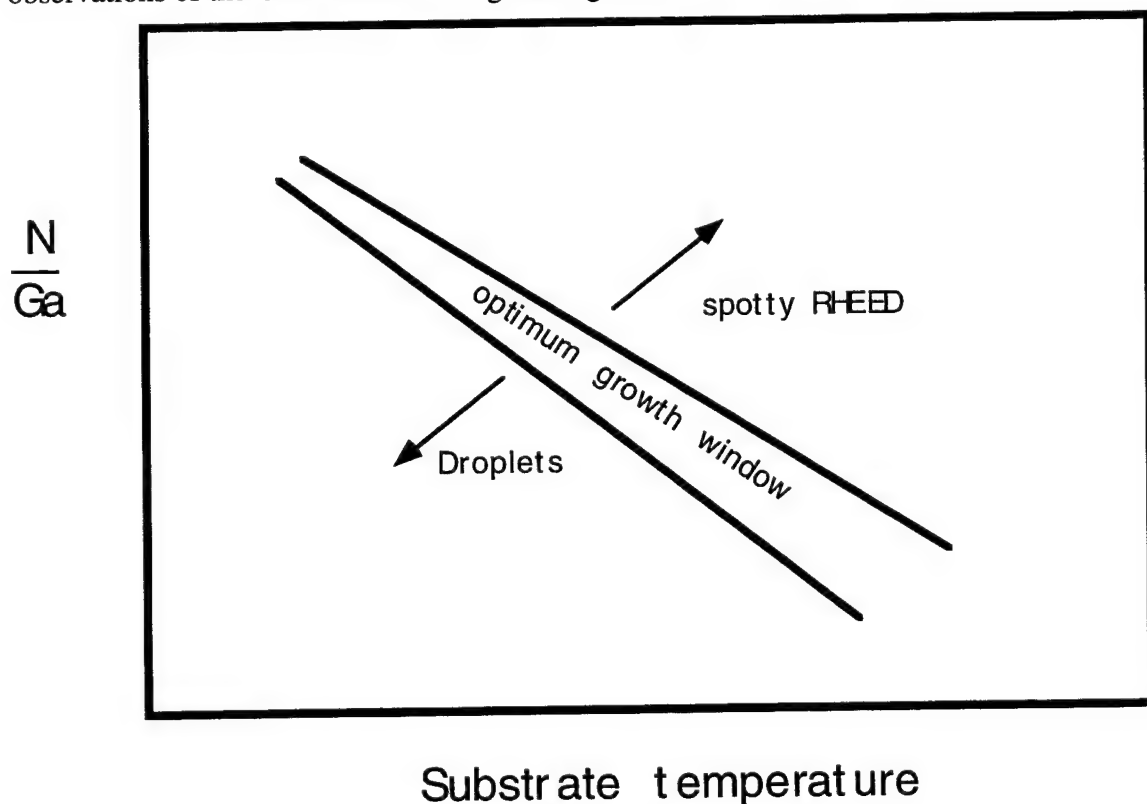


Figure 4 Diagram showing regimes of different behaviors seen over the growth parameters for MBE grown GaN

For a given temperature, the effect of changing the atomic to Ga ratio can be significant. At high Ga fluxes, or low atomic fluxes, the RHEED pattern can look very good - clear, strong streaks which are similar to what is seen for GaAs growth. Photoluminescence is strongest for the smallest ratios. The surface, however, is covered with Ga droplets and is not usable for device fabrication. The droplets are a few microns in diameter, and their density can be anywhere from a few percent coverage of the surface up to almost 50% coverage. Hall measurements cannot be performed on the discontinuous islands of GaN between the droplets. When the ratio is changed towards higher values, the RHEED pattern is spotty, however surfaces are continuous and there are no droplets. GaN grown under this condition often produces layers which are sufficiently conducting for making Hall measurements.

When substrate temperature is lowered, either the Ga flux must be lowered, or the atomic N flux must be increased to avoid droplet formation. The limits for these observations are not yet known. At temperatures as low as 700°C (thermocouple), the RHEED pattern can look amorphous when the Ga flux is too high. This temperature may be part of some other regime which is yet to be determined. Another regime seems to exist where the atomic N flux is absent. Here, no growth takes place, and no droplets are observed! This condition should be where highest droplet densities are observed based on all other observations. Clearly, the growth kinetics for RF plasma

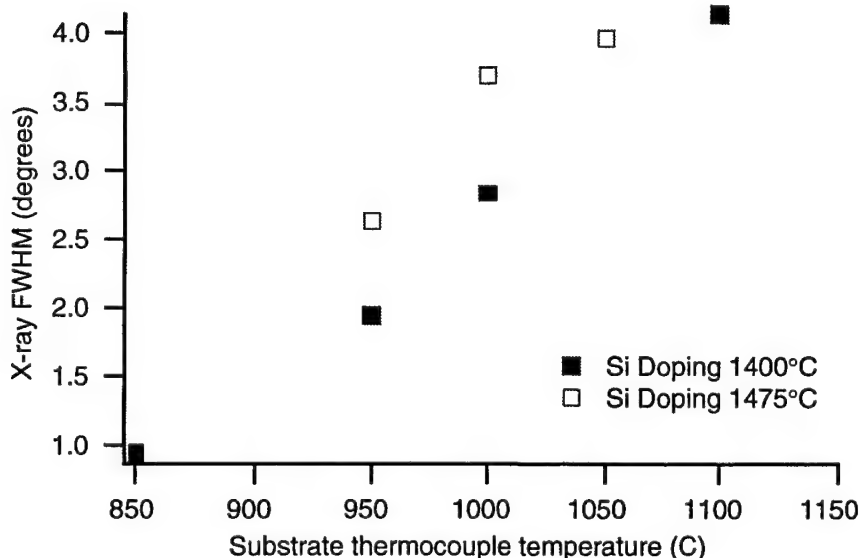


Figure 5 Change in AlN X-Ray FWHM as a function of substrate thermocouple temperature for two different Si doping furnace temperatures.

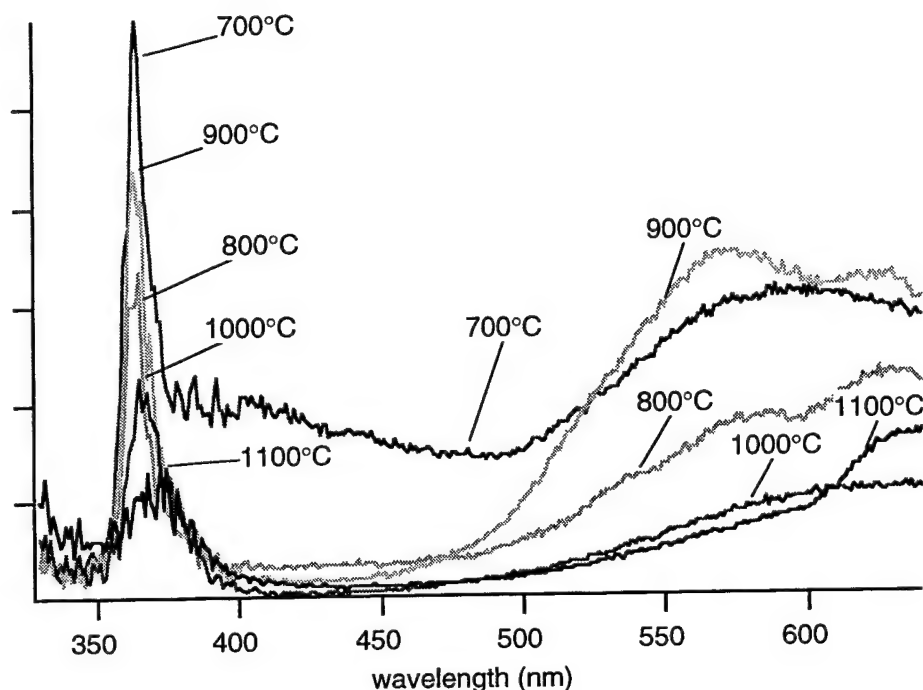
source atomic nitrogen growth of GaN are not yet understood. Many of the observations for atomic nitrogen source growth are similar to those obtained by ECR sources of active nitrogen that are used for MBE growth.

AlN buffer growth

A series of growths were performed where

the GaN buffer was replaced by an AlN buffer grown at different substrate temperatures. The substrate temperature range explored was chosen following earlier experience with growth of AlN at different substrate temperatures. The quality of AlN as a function of substrate temperature is in Figure 5. From the trend seen, it would be expected that at lower temperature, undoped AlN would be of much higher quality than what was measured in this study of AlN epitaxy.

In an effort to obtain the highest AlN quality for application to the study of AlN buffers for GaN, thermocouple temperatures as low as 700°C were used. (Note - actual substrate temperatures are approximately 200°C lower than thermocouple temperatures). The goal of the study was to determine if the mobility and PL of GaN would be a function of the quality of the AlN buffer.



300K PL from GaN as a function of the AlN nucleation substrate temperature

Prior to growth, the sapphire substrates were ramped to a thermocouple temperature of 1050°C and then exposed to 350W plasma for 3 minutes. The N_2 pressure in the chamber was nominally 1×10^{-6} Torr with a flow of ~ 2.5 sccm. The substrate temperature was lowered prior to AlN growth. Approximately 100 Å of AlN was grown at ~ 0.1 $\mu\text{m}/\text{hour}$ rate on the sapphire substrate. After a 3

minute anneal, AlN was grown at this temperature at a growth rate of about 0.1 $\mu\text{m/hr}$ for approximately 500 \AA . Another interruption took place while the substrate temperature was set to 960°C for 12 hours of growth.

From the PL data, some trend in bandgap luminescence is seen. Higher substrate temperatures for AlN buffers seems to cause the band-edge PL intensity of GaN to fall. This would seem to be in agreement with the study of AlN on sapphire. The poorer quality AlN provides a poorer nucleation layer for GaN growth. Mobility also seems to follow this trend where the highest mobility for GaN on AlN that was grown at the lowest temperature. For higher nucleation layer substrate temperatures, they do not follow the same relationships as seen for PL. It is interesting to note that the highest mobility GaN (700°C AlN buffer) has both the highest PL intensity at bandedge, and the highest yellow PL emission. The highest mobilities also occur for the lowest carrier densities. This behavior is similar, but not as well correlated as that seen for doped GaN where only doping concentration is varied. The carrier densities of the AlN buffered GaN were not as expected. For the same structure with a GaN buffer the carrier concentration would be approximately $5 \times 10^{17} \text{ cm}^{-3}$.

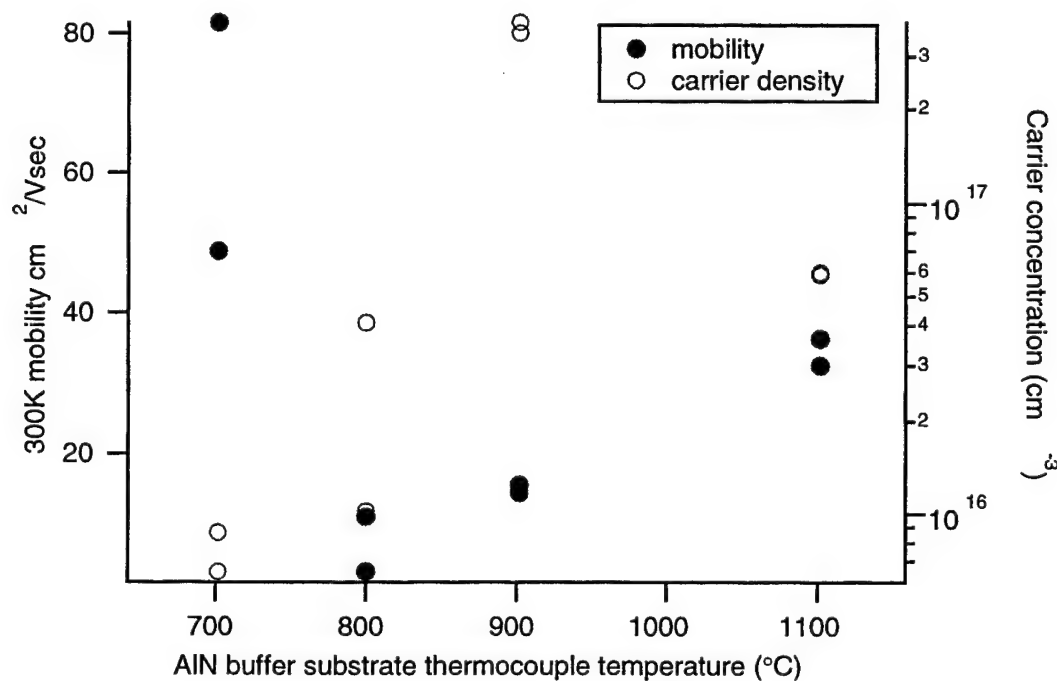


Figure 6 Mobility and electron concentration of GaN as a function of AlN nucleation layer substrate temperature

In contrast to PL from GaN grown on AlN, PL from GaN on low temperature GaN nucleation layers is seen in Figure 7. The band edge PL is very strong while defect luminescence at yellow wavelengths is significantly reduced. The strong band edge PL indicates that there is high radiative recombination efficiency. The quality indicated by this PL is probably sufficient for fabrication of GaN lasers. The PL shown is from a sample with better than average PL strength. Typical GaN has bandedge to yellow band intensity ratios of around 100 using our measurement system.

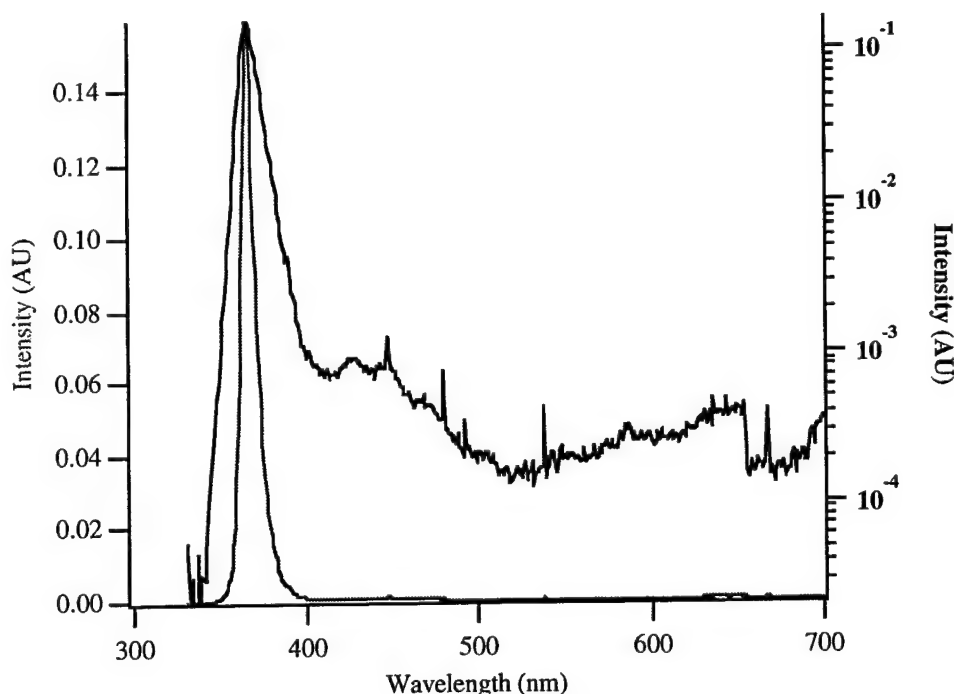


Figure 7 300K PL from GaN on linear and log axes

Plasma RF source degradation

A new form of remote RF plasma source was installed at the end of the program. A Uni-bulb source from EPI uses one piece construction for improved atomic N generation efficiency. In a few dozen growths, it has been used to reliably grow GaN at rates of $0.6\mu\text{m/hr}$ compared to a maximum from the previous source of $0.2\mu\text{m/hr}$. Mobilities are also higher. For doping of $1 \times 10^{18} \text{ cm}^{-3}$, the EPI source produces 300K mobilities between 200 and $300 \text{ cm}^2/\text{Vsec}$, while the Oxford source could not grow materials with mobilities beyond 160. Both sources, however, exhibit an undesirable degradation in performance over a time period as short as one month of continuous use. We think we can explain this behavior based on a model of PBN liner erosion.

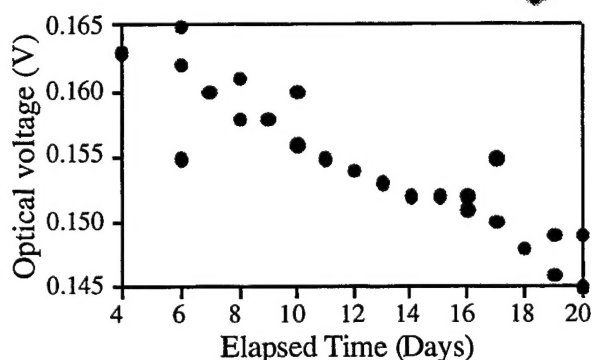
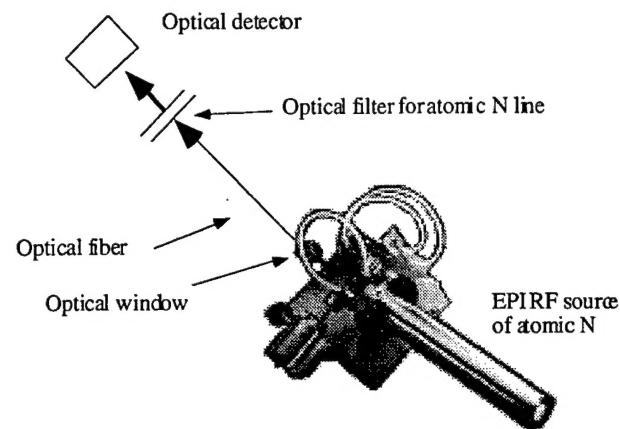


Figure 8 Degradation of optical voltage corresponding to atomic nitrogen

to decreased atomic nitrogen generation efficiency. The reason for the fall in efficiency is because of erosion of the PBN liner which results in dark streaks thought to be boron around the inside perimeter of the PBN liner. A sketch of the liner as seen in the Oxford source is seen in Figure 9.

The best reproducible buffer layer recipe was found to require two ingredients - low growth rate, and high temperature anneal. Nucleation layers are initiated at low growth rates, and growth rate is ramped up to $0.2\mu\text{m/hr}$. Anneal at thermocouple temperatures near 1200°C for 15 minutes to 1 hour is then performed prior to lowering the substrate thermocouple temperature to 973°C for epitaxial growth. When these steps are followed, the RHEED image during the growth of the doped layer

Atomic nitrogen present in the source can be monitored through the observation of the optical spectrum of the plasma glow. Optical filters to reject all wavelengths of light except those that come from atomic nitrogen transition lines are used in front of an optical detector. The detector output is directly proportional to the amount of atomic nitrogen present in the plasma. The atomic nitrogen signal is dependent on RF power, the amount of nitrogen that is injected into the source, and the source efficiency.

This signal has been plotted for the EPI source which was installed just after the end of the program. It can be seen in Figure 8 that the optical signal intensity falls with time. It is thought that the reason for this fall is due

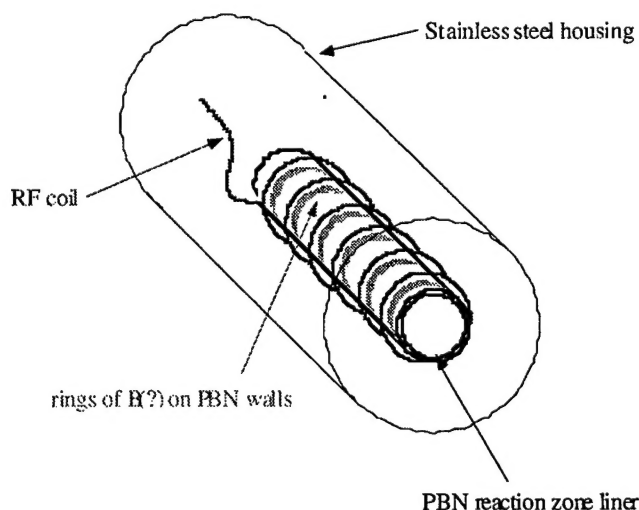


Figure 9 Sketch of PBN liner in Oxford RF source showing dark rings

quickly becomes very streaky, and clear Kikuchi lines are seen. These RHEED patterns are the closest to those of GaAs for GaN growth in this lab. Other growth conditions produce RHEED with different magnitudes of spotty content.

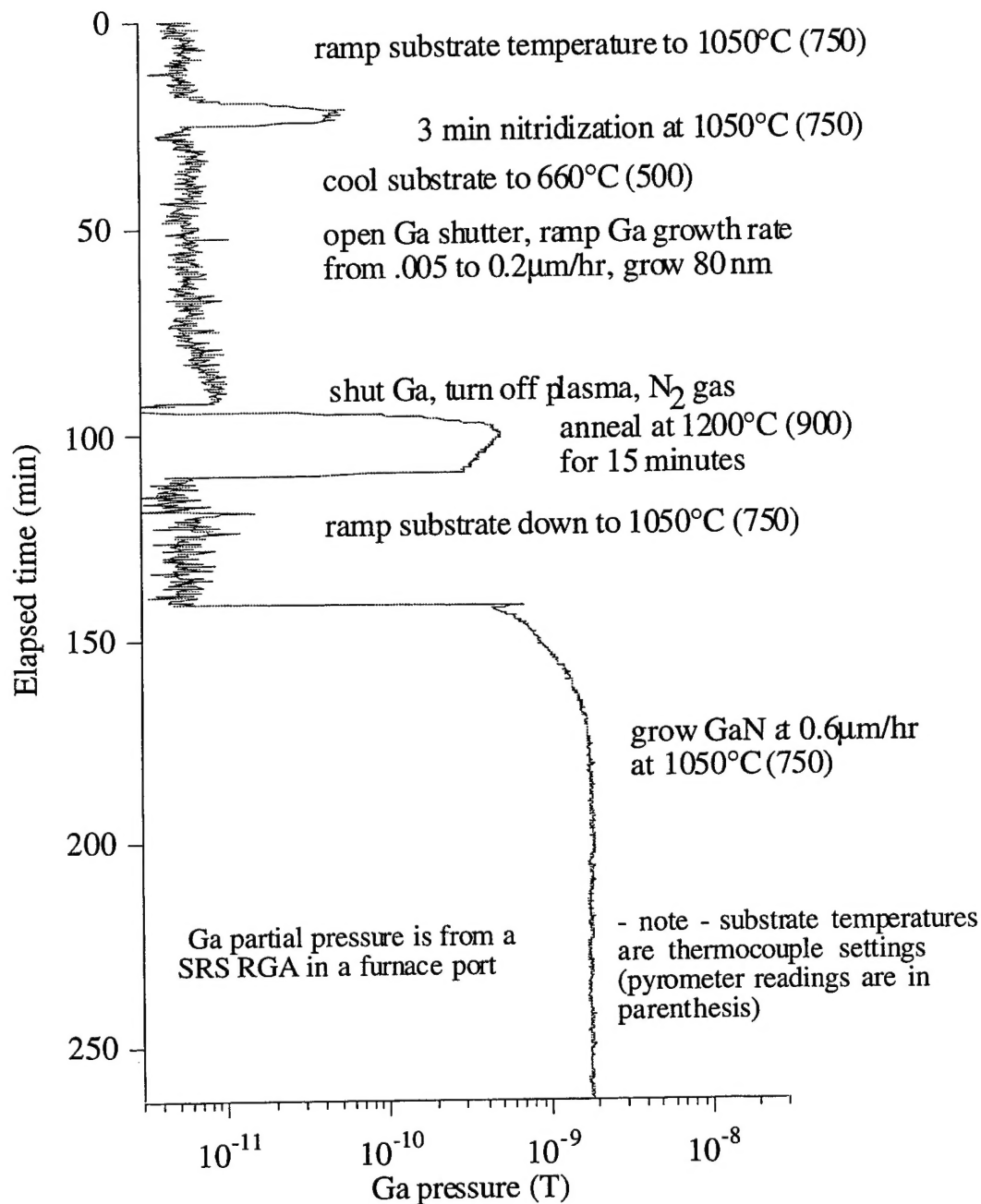


Figure 10 Growth recipe superimposed on Ga desorption as measured by a residual gas analyzer

A graphical representation of the growth recipe for GaN on sapphire is shown in Figure 10. It is superimposed on the Ga desorption data taken by a residual gas analyzer located in a furnace port. Approximately 2 hours is dedicated to producing an optimum nucleation layer. The substrate is nitridized for 3 minutes at high temperature, then growth takes place at low temperature while starting at a low growth rate. After a nucleation layer is established, the layer is annealed at high temperature. After anneal, GaN is then grown for device or characterization applications.

The desorption data seen in Figure 10 has some interesting features. It is clear that desorption of Ga from GaN is not constant with time - it falls during the high temperature anneal. There may be a self-limiting process occurring. As the GaN thickness decreases, the absorption of black body heat from the heater falls, the surface cools, the bandgap rises and further reduces absorption. During the growth of GaN following the anneal, it can be seen that the Ga desorption varies with time. The same argument can be applied here. As the GaN layer becomes thicker, it absorbs more black body radiation from the hot surfaces below, becomes warmer, its bandgap shrinks and thereby raises absorption of more of the black body radiation. Eventually, thickness does not play a role in epi-layer temperature when the layer is several absorption lengths thick. The non-constant surface temperature makes optimization of GaN growth a significant problem. In-situ techniques to monitor GaN temperature such as PL and reflectance/absorption are needed.

Summary

The growth of GaN by MBE for application to blue and UV lasers has produced new understanding of the growth process. Despite the lack of a lattice matched substrate, GaN with very high quality as determined by electrical and optical measurements has been demonstrated. A critical element of MBE growth is the efficiency of the RF plasma source of atomic nitrogen. The design of commercial RF sources presently available is inadequate for development of GaN lasers grown by MBE. Although significant progress has been seen in use of second generation sources, crucible degradation remains a serious problem.

Optimization of growth conditions has included study of substrate temperature and nucleation layer parameters. High substrate temperatures are seen to be important for best electrical properties, and GaN nucleation layers produce superior device GaN compared to using AlN nucleation layers. A better source of atomic nitrogen would lead to higher growth rates, better electrical properties, and possibly permit lower substrate temperature growth. All of these developments are important for commercial GaN laser development.

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